

CLAIMS:

1. A process for preparing an olefin polymerization catalyst comprising:
- A. calcining silica at a temperature of 30 to 1000°C to form calcined silica,
 - B. reacting the calcined silica with an agent selected from the group consisting of:
 - i. Lewis acid alkylating agents,
 - ii. silane or chlorosilane functionalizing agents, and
 - iii. aluminum components selected from an alumoxane or an aluminum compound of the formula $AlR^1_xR^2_{y'}$, wherein R^1 independently each occurrence is hydride or R, R^2 is hydride, R or OR, x' is 2 or 3, y' is 0 or 1 and the sum of x' and y' is 3, to form a support precursor having a specified pore volume,
 - C. applying to the support precursor a first solution in a compatible solvent of one of the following:
 - (1) a complex of a metal of Groups 3-10 of the Periodic Table of the Elements or
 - (2) a cocatalyst selected from the group consisting of non-polymeric, non-oligomeric complexes capable of activating the complex of (C)(i) for the polymerization of α -olefinsand optionally removing the compatible solvent to form a supported procatalyst;
 - D. applying to the supported procatalyst a second solution in a compatible solvent of the other of the catalyst or cocatalyst of (C) to form a supported catalyst, wherein the second solution is provided in an amount such that 100 percent of the pore volume of the support precursor is not exceeded; and
 - E. optionally removing the compatible solvent from the supported catalyst to form a recovered supported catalyst system.

2. The process of Claim 1, wherein the first solution of (C) is provided in an amount not in excess of 100 percent of the pore volume of the support precursor, and wherein the compatible solvent of step (C) is removed from the supported procatalyst by heating, subjecting to reduced pressure, or a combination thereof.

3. The process of Claim 1, wherein the first solution of (C) is provided in an amount not in excess of 100 percent of the pore volume of the support precursor, and wherein the optional removal of compatible solvent of step (C) is not employed.
4. The process of Claim 1, wherein step (C) further comprises:
 - (i) forming a slurry of the support precursor in the compatible solvent,
 - (ii) adding to the slurry, the complex of step (C)(1) or the cocatalyst of step (C)(2) to form a procatalyst slurry, and
 - (iii) removing the compatible solvent from the procatalyst slurry to form the supported procatalyst.

5. The process of Claim 1, wherein the Group 3-10 metal complex is $L MX_m X'_n X''_p$, or a dimer thereof wherein:

L is an anionic, delocalized, π -bonded group that is bound to M, containing up to 50 nonhydrogen atoms, optionally two L groups may be joined together through one or more substituents thereby forming a bridged structure, and further optionally one L may be bound to X through one or more substituents of L;

M is a metal of Group 4 of the Periodic Table of the Elements in the +2, +3 or +4 formal oxidation state;

X is an optional, divalent substituent of up to 50 non-hydrogen atoms that together with L forms a metallocycle with M;

X' is an optional neutral Lewis base having up to 20 non-hydrogen atoms;

X'' each occurrence is a monovalent, anionic moiety having up to 40 non-hydrogen atoms, optionally, two X'' groups may be covalently bound together forming a divalent dianionic moiety having both valences bound to M, or form a neutral, conjugated or nonconjugated diene that is π -bonded to M (whereupon M is in the +2 oxidation state), or further optionally one or more X'' and one or more X' groups may be bonded together thereby forming a moiety that is both covalently bound to M and coordinated thereto by means of Lewis base functionality;

l is 1 or 2;

m is 0 or 1;

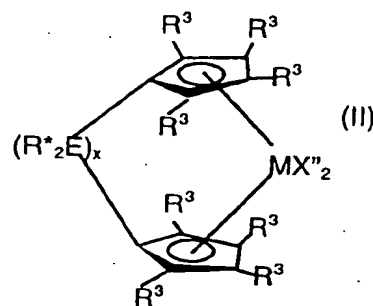
n is a number from 0 to 3;

p is an integer from 0 to 3; and

the sum, $l+m+p$, is equal to the formal oxidation state of M.

6. The process of Claim 5, wherein the Group 3 - 10 metal complex contains two L groups which are linked by a bridging group, wherein the bridging group corresponds to the formula $(ER^*_2)_x$, wherein E is silicon or carbon, R^*

(I)



or

M is titanium, zirconium or hafnium, preferably zirconium or hafnium, in the +2 or +4 formal oxidation state;

R^3 in each occurrence independently is selected from the group consisting of hydrogen, hydrocarbonyl, silyl, germyl, cyano, halo and combinations thereof, said R^3 having up to 20 non-hydrogen atoms, or adjacent R^3 groups together form a divalent derivative (that is, a hydrocarbadiyl, siladiyl or germadiyl group) thereby forming a fused ring system, and

X" independently each occurrence is an anionic ligand group of up to 40 nonhydrogen atoms, or two X" groups together form a divalent anionic ligand group of up to 40 nonhydrogen atoms or together are a conjugated diene having from 4 to 30 non-hydrogen atoms forming a π -complex with M, whereupon M is in the +2 formal oxidation state, and

R^* , E and x are as previously defined.

8. The process of Claim 1, wherein the Group 3 - 10 metal complex corresponds to the formula:

$$L_1MX_mX'_nX''_p, \text{ or a dimer thereof}$$

wherein:

L is an anionic, delocalized, π -bonded group that is bound to M, containing up to 50 nonhydrogen atoms;

M is a metal of Group 4 of the Periodic Table of the Elements in the +2, +3 or +4 formal oxidation state;

X is a divalent substituent of up to 50 non-hydrogen atoms that together with L forms a metallocycle with M;

X' is an optional neutral Lewis base ligand having up to 20 non-hydrogen atoms;

X" each occurrence is a monovalent, anionic moiety having up to 20 non-hydrogen atoms, optionally two X" groups together may form a divalent anionic moiety having both valences bound to M or a neutral C₅₋₃₀ conjugated diene, and further optionally X' and X" may be bonded together thereby forming a moiety that is both covalently bound to M and coordinated thereto by means of Lewis base functionality;

l is 1 or 2;

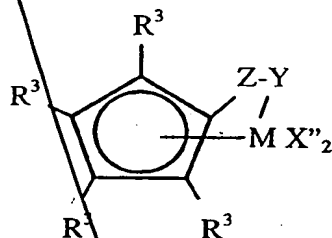
m is 1;

n is a number from 0 to 3;

p is an integer from 1 to 2; and

the sum, l+m+p, is equal to the formal oxidation state of M.

9. The process of Claim 8, wherein the metal complex corresponds to the formula:



wherein:

M is titanium or zirconium in the +2 or +4 formal oxidation state;

R³ in each occurrence independently is selected from the group consisting of hydrogen, hydrocarbyl, silyl, germyl, cyano, halo and combinations thereof, said R³ having up to 20 non-hydrogen atoms, or adjacent R³ groups together form a divalent derivative (that is, a hydrocarbadiyl, siladiyl or germadiyl group) thereby forming a fused ring system,

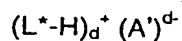
each X" is a halo, hydrocarbyl, hydrocarbyloxy or silyl group, said group having up to 20 nonhydrogen atoms, or two X" groups together form a C₅₋₃₀ conjugated diene;

Y is -O-, -S-, -NR*, -PR*; and

Z is SiR*₂, CR*₂, SiR*₂SiR*₂, CR*₂CR*₂, CR*=CR*, CR*₂SiR*₂, or GeR*₂,

wherein: R* is as previously defined.

10. The process of Claim 1, wherein the cocatalyst is represented by the formula



wherein:

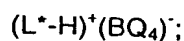
L^* is a neutral Lewis base;

$(L^*-H)^+$ is a Bronsted acid;

A'^{d-} is a noncoordinating, compatible anion having a charge of d^- , and

d is an integer from 1 to 3.

11. The process of Claim 1, wherein the cocatalyst is represented by the formula:



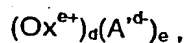
wherein:

L^* is a neutral Lewis base;

B is boron in a formal oxidation state of 3; and

Q is a hydrocarbyl-, hydrocarbyloxy-, fluorinated hydrocarbyl-, fluorinated hydrocarbyloxy-, or fluorinated silylhydrocarbyl- group of up to 20 nonhydrogen atoms, with the proviso that in not more than one occasion is Q hydrocarbyl.

12. The process of Claim 1, wherein the cocatalyst comprises a salt of a cationic oxidizing agent and a noncoordinating, compatible anion represented by the formula:



wherein,

Ox^{e+} is a cationic oxidizing agent having a charge of e^+ ;

e is an integer from 1 to 3; and

A^{d-} is a noncoordinating, compatible anion having a charge of d-, and

d is an integer from 1 to 3.

13. The process of Claim 1, wherein the cocatalyst comprises a salt of a carbenium ion and a noncoordinating, compatible anion represented by the formula:

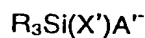


wherein:

C⁺ is a C₁₋₂₀ carbenium ion; and

A⁻ is a noncoordinating, compatible anion having a charge of -1.

14. The process of Claim 1, wherein the cocatalyst comprises a compound which is a salt of a silylium ion and a noncoordinating, compatible anion represented by the formula:



wherein:

R is C₁₋₁₀ hydrocarbyl;

X' is hydrogen or R; and

A⁻ is a noncoordinating, compatible anion having a charge of -1.

15. The process of Claim 1, wherein the support precursor is characterized as having a pore volume, as determined by nitrogen adsorption, of from 0.1 to 3 cm³/g.

16. The process of Claim 1, wherein the reacting of the calcined silica with the agent comprises:

- (a) adding to the calcined silica sufficient solvent to achieve a slurry;
- (b) adding to the slurry the agent in an amount of 0.1 to 5 mmol agent per gram of calcined silica, to form a treated support;
- (c) washing the treated support to remove unreacted agent to form a washed support, and

- (d) drying the washed support by heating and/or by subjecting to reduced pressure.

17. The process of Claim 1, wherein the support precursor is characterized as having a residual hydroxyl content of less than 2 mmol of OH per gram of support precursor.

18. The process of Claim 1, wherein at least one of the supported procatalyst or the supported catalyst is treated by at least one of the following:

- a. applying thereto a vacuum of from 0.05 to 150 Torr; or
- b. heating to a temperature of from 0 to 60°C.

19. A process for polymerizing at least one α -olefin monomer comprising:

A. preparing a supported cocatalyst by:

- i. calcining silica at a temperature of 30 to 1000°C to form calcined silica,
- ii. reacting the calcined silica with an agent selected from the group consisting of:
 - (a) Lewis acid alkylating agents,
 - (b) silane or chlorosilane functionalizing agents, and
 - (c) aluminum components selected from an alumoxane or an aluminum compound of the formula $AlR^1_xR^2_y$, wherein R^1 independently each occurrence is hydride or R, R^2 is hydride, R or OR, x' is 2 or 3, y' is 0 or 1 and the sum of x' and y' is 3,

to form a support precursor having a specified pore volume, applying to the support precursor a first solution in a compatible solvent of one of the following:

- (a) a complex of a metal of Groups 3-10 of the Periodic Table of the Elements or
- (b) a cocatalyst selected from the group consisting of non-polymeric, non-oligomeric complexes capable of activating the complex of (C)(i) for the polymerization of α -olefins

- and optionally removing the compatible solvent to form a supported procatalyst;
- iv. applying to the recovered supported procatalyst a second solution in a compatible solvent of the other of the catalyst or cocatalyst of (C) to form a supported catalyst, wherein the second solution is provided in an amount such that 100 percent of the pore volume of the support precursor is not exceeded; and
- v. optionally removing the compatible solvent from the supported catalyst to form a recovered supported catalyst system;
- B. pressurizing a gas phase polymerization reactor with the at least one α -olefin monomer to be polymerized;
- C. introducing the recovered supported catalyst system to the gas phase polymerization reactor;
- D. activating the recovered supported catalyst system; and
- E. recovering the polymerized product from the reactor.
20. The process of Claim 19, further comprising providing to the reactor a tri(hydrocarbyl)aluminum compound having from 1 to 10 carbons in each hydrocarbyl group, an oligomeric or polymeric alumoxane compound, a di(hydrocarbyl)(hydrocarbyloxy)aluminum compound having from 1 to 10 carbons in each hydrocarbyl or hydrocarbyloxy group, or a mixture of the foregoing compounds, wherein such providing occurs either prior to, during, or subsequent to the introduction to the reactor of the recovered supported catalyst system.